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Critical Evaluation of Differential Pulse Polarography for Determining Chromium(III) and Chromium(VI) in Water Samples

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Critical Evaluation of Differential Pulse Polarography for Determining Chromium(III) and Chromium (VI) in Water Samples

Interagency Energy/Environment R&D Program Report

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The Tennessee Valley Authority critically evaluated differential pulse polarography for determining chromium(VI) and chromium (III) in water samples from coal-fired steam-electric generating stations. After addition of reagents to overcome interference, the peak currents for chromium(III) and chromium(VI) are measured separately in different electrolytes and quantified by standard addition. Total chromium is the algebraic sum of chromium(VI) and chromium(III). The effective range for quantification is 0.1 to 10 mg/l of chromium(VI) and 0.6 to 10 mg/l of chromium(III). Interferences by lead(II) and chromium(VI) on chromium(III) are discussed. Lead(II) does not interfere with measurement of chromium(VI), and chromium(III) does not interfere with chromium(VI). Copper(II), zinc(II), and iron(III) do not interfere with measurement of either chromium(III) or chromium(VI).

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CRITICAL EVALUATION OF DIFFERENTIAL PULSE POLAROGRAPHY FOR DETERMINING CHROMIUM(III) AND CHROMIUM(VI) IN WATER SAMPLES

by

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ABSTRACT

The Tennessee Valley Authority critically evaluated differential pulse polarography for determining chromium(VI) and chromium(III) in water samples from coal-fired steam-electric generating stations. After reagents are added to overcome interference, the peak currents for chromium(III) and chromium(VI) are measured separately in different electrolytes and quantified by standard addition. Total chromium is the algebraic sum of chromium(VI) and chromium(III). The effective range for quantification is 0.1 to at least 10 mg/l of chromium(VI) and 0.6 to at least 10 mg/l of chromium(III). Interferences by lead(II) and chromium(VI) on chromium(III) are discussed. Neither lead(II) nor chromium(III) interferes with measurement of chromium(VI). Copper(II), zinc(II), and iron(III) do not interfere with measurement of either chromium(III) or chromium(VI).

This report was submitted by the Tennessee Valley Authority, Office of Natural Resources, in partial fulfillment of Energy Accomplishment Plan 79BDH under terms of Interagency Energy Agreement D5-E721 with the Environmental Protection Agency. Work was completed in October 1978.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

A	--ampere
c	--centi-, $x10^{-2}$ (as a prefix, e.g., cm)
°C	--degrees Celsius (centigrade)
DPP	--differential pulse polarography
EDTA	--ethylenediaminetetraacetic acid
EPA	--U.S. Environmental Protection Agency
g	--grams
hr	--hour
in.	--inch
l	--liter
m	--meter
m-	--milli-, $x10^{-3}$ (as a prefix, e.g., mm)
min	--minute
M	--molar, mole per liter
NBS	--National Bureau of Standards
psi	--pound per square inch
PAR	--Princeton Applied Research Corporation
s	--second
t	--student t statistic
TVA	--Tennessee Valley Authority
V	--volt
V vs. nce	--volts vs. a calomel electrode filled with 1 M potassium chloride

SYMBOLS

μ-	--micro-, $x10^{-6}$ (as a prefix, e.g., μg)
%	--percent

SECTION 1

INTRODUCTION

Chromate, the highest valence state for chromium, has potential for use as a corrosion inhibitor in process waters for heat exchangers and in other service water systems at steam-electric generating stations.[1] Chromate may also be deposited in aqueous wastes that are formed when heat exchangers are cleaned with acid solvents or that are extracted when coal ash is sluiced with water into settling ponds. Even though hexavalent chromium, including the lower trivalent species, can be removed by adsorption,[2,3] precipitation,[4,5] or recycling,[6] some may eventually reach surface or ground waters.

Tandon[7] concluded recently that, although damage to kidneys in rabbits by hexavalent chromium far exceeds that by trivalent chromium, care must also be taken to avoid trivalent chromium compounds, particularly those that are water-soluble. The purpose of this work, funded by an interagency agreement by TVA under sponsorship of EPA, is to examine polarography as a possible means for determining chromium(VI) and chromium(III) concentrations individually.

As required by the Federal Water Pollution Control Act, test procedures have been published for determining concentrations of total and hexavalent chromium by atomic absorption or colorimetry to demonstrate that effluent discharges meet applicable pollutant discharge limitations.[8] Although not a compliance method, the determination of chromium by differential pulse polarography is attractive because it offers a potential means for quantifying chromium(VI) and chromium(III) individually, with a sensitivity of about 1/20 of that for direct-current polarography.[9-12] Valence-specific methods for determining concentrations of hexavalent and trivalent chromium, including polarography, and the significance of these measurements in biological systems have been reviewed by Purdy[13] and Mertz.[14]

Sodium hydroxide has been used to determine chromium(VI) concentrations by differential pulse polarography[15,16] and by direct-current polarography.[17,18] The usefulness of this electrolyte in a concentration of 1 M is limited by interference from lead(II) and an increase in peak height thought to be caused by the peroxide formed when the dropping mercury electrode is placed in solution during deaeration.[15] Crosmun and Mueller[19] resolved these limitations by determining chromium(VI) in a different electrolyte, 0.1 M acetate buffer with 5×10^{3} M ethylenediamine at pH 7. For this report, sodium hydroxide in a concentration of 0.1 M was selected instead of the 1 M concentration for evaluation as an electrolyte for determining chromium(VI). It was hoped that the 0.1 M concentration might eliminate peroxide formation and interference by lead without lowering the pH sufficiently to allow interference by copper.[15]

Several electrolytes have been recommended for determining chromium(III) concentrations by polarography.[20-24] Information for interferences in the determination of chromium(III) is available only for two electrolytes: (1) 0.2 M acetic acid with 0.2 M sodium thiocyanate at pH 3.2;[21,22] and (2) 0.1 M potassium chloride with 0.01 M ethylenediaminetetraacetic acid (EDTA) at pH 6.[24] Although not specifically mentioned in the literature,[21,22,24] thiocyanate[21,22] or EDTA[24] is probably required to maintain chromium(III) in solution by complexing. Both zinc(II) and chromium(VI) cause some indirect interference by shifting the baseline when chromium(III) concentrations are determined in 0.2 M acetic acid with 0.2 M sodium thiocyanate at pH 3.2.[21,22] Preliminary data in the TVA laboratory showed that copper(II) also produces similar results. Because further preliminary results in the TVA laboratory indicated that the baseline was not shifted by copper(II) and zinc(II) when chromium(III) concentrations were determined in 0.2 M ammonium citrate with 0.01 M EDTA at pH 5, this electrolyte was chosen for detailed evaluations for quantifying chromium(III). Some interference by chromium(VI) was observed, but it was less than that for 0.1 M potassium chloride with 0.01 M EDTA at pH 6.0, because in this electrolyte, the peaks for chromium(III) and chromium(VI) coincide.[24]

This report evalutes the effect of

1. pH, zinc(II), iron(III), copper(II), lead(II), and chromium(III) in determining concentrations of chromium(VI) in 0.1 M sodium hydroxide by differential pulse polarography; and

2. pH, zinc(II), iron(III), copper(II), lead(II), and chromium(VI) in determining concentrations of chromium(III) in 0.2 M ammonium citrate with 0.01 M EDTA.

SECTION 2

CONCLUSIONS

A differential pulse polarographic method has been critically evaluated for determining chromium(VI) and chromium(III) concentrations in natural water samples. Differential pulse polarography is effective for determining 0.1 to at least 10 mg/l of chromium(VI) and 0.6 to at least 10 mg/l of chromium(III).

Chromium(VI) is measured at about -1.14 V vs. nce at pH 12.7 in 0.1 M sodium hydroxide. The height and potential of the chromium(VI) reduction peak are nearly the same at pH 11.7 and 12.7. At pH 13.2, the peak height is the same as at pH 11.7 and 12.7, but the potential is -0.95 V vs. nce rather than -1.15 V. Chromium(III) is measured at about -1.26 V vs. nce at pH 5.0 in 0.2 M ammonium citrate buffer solution with 0.01 M EDTA. The potential of the chromium(III) peak is the same at pH values between 4.7 and 5.2. The height of the peak is the same at pH 4.7 and 5.0, but at pH 5.2 it is 43 percent of the value at pH 5.0.

A concentration of 5.0 mg/l of copper(II), zinc(II), and iron(III) does not interfere with measurement of either chromium(III) or chromium(VI), and a concentration of 5.0 mg/l of lead(II) and chromium(III) does not interfere with measurement of chromium(VI). However, a concentration of 5 mg/l of lead(II) and chromium(VI) does interfere with measurement of chromium(III).

SECTION 3

RECOMMENDATIONS

The differential pulse polarographic method described in this report lacks the sensitivity for directly determining the low concentrations of total chromium, chromium(VI), and chromium(III) that are normally expected in ash ponds that receive effluents from steam-electric generating plants.[25] This method may be applicable to the determination of chromium(VI) and chromium(III) in industrial effluents or process waters containing higher concentrations of chromium. This, of course, remains to be proven because of the possible presence of various interferences in such samples.

Further studies should be conducted to determine the applicability of the differential pulse polarographic method described in this report for low concentrations of chromium(VI) and chromium(III) after preconcentration of chromium(VI) by ion exchange[26] and of chromium(III) by coprecipitation with iron(III) hydroxide.[27]

SECTION 4

EXPERIMENTAL

SAMPLE PREPARATION

Standard Reference Sample

A standard reference sample, consisting of known amounts of concentrated trace metals in very pure water, was obtained from EPA. The reference sample was diluted to the desired concentration according to accompanying instructions.[28]

Synthetic Samples

Test solutions containing 0, 0.05, 0.1, 0.3, 0.5, and 1.0 of chromium(III) or chromium(VI) were prepared by spiking exactly 5 or 9 ml of very pure water in a series of 50-ml Pyrex beakers with 0, 5, 10, 30, 50, and 100 µl of a 100-mg/l standard of chromium(III) or chromium(VI). After the chromium solutions were mixed, exactly 5 ml of 0.4 M ammonium citrate buffer with 0.02 M EDTA (pH 5.0) was added to the chromium(III), and exactly 1 ml of 1 M sodium hydroxide was added to the chromium(VI). Test solutions containing 2.0, 5.0, 7.5, and 10 mg/l chromium(III) and chromium(VI) were prepared similarly by spiking with 20, 50, 75, and 100 µl of a 1000-mg/l standard of chromium(III) or chromium(VI). The 5-mg/l concentrations of zinc(II), copper(II), lead(II), chromium(III), chromium(VI), and iron(III) were prepared similarly, too, by spiking with 50 µl of a 1000-mg/l standard solution of the respective element. After being mixed, the solutions were transferred to the cell for the polarographic measurements.

All elements used to prepare synthetic samples, except iron(III), chromium(III), and chromium(VI), were drawn from 1000-mg/l certified atomic absorption standards (Fisher Scientific Company, Fairlawn, New Jersey). The 1000-mg/l concentration of iron(III) was prepared gravimetrically from ferric ammonium sulfate-12-water (8.634 g in 1000 ml of reagent water) with weights checked against reference weights traceable to the National Bureau of Standards (NBS). The 1000-mg/l concentration of chromium(III) was prepared by dissolving exactly 0.7696 g of chromium(III) nitrate-9-water in reagent water and diluting to 100 ml in a volumetric flask. The 1000-mg/l concentration of chromium(VI) was prepared by dissolving exactly 0.2828 g of anhydrous potassium dichromate with dilution to 100 ml in a volumetric flask.

EQUIPMENT

All measurements were made with the Princeton Applied Research (PAR) model 174 polarographic analyzer with mechanical drop timer and Houston omnigraphic X-Y recorder model 2200-3-3. The dropping mercury electrode was a 2- to 5-s capillary from Sargent-Welch Company with part no. S-29419.

Other instruments--the platinum counter electrode; the calomel electrode; the salt bridge with slow-leakage Vycor tip (Corning Glass Works, Corning, New York) for isolating the calomel electrode from the test solution; the outgassing tube; cell holder; and cell--were obtained from Princeton Applied Research Corporation.[29] An adjustable digital microliter pipette (Analtech, Newark, Delaware, part no. P-20D or P-200D) was used to spike solutions.

PREPARATION OF EQUIPMENT AND SOLUTIONS

Glassware that contacted the sample solution was soaked overnight in a solution of two volumes of concentrated nitric acid in three volumes of water. After leaching, the glassware was rinsed with reagent water and dried in an oven at 110°C. Clean glassware and solutions were covered with Parafilm (Fisher Scientific Company, Fairlawn, New Jersey) to prevent contamination from trace elements in atmospheric particles.

Nitrogen gas, used to deaerate solutions for polarographic analysis, was purged of oxygen. Zero-grade nitrogen gas was passed through a furnace containing a special catalytic converter (a gas purifier, model 02-2315, purchased from Supelco, Bellefonte, Pennsylvania) and heated to 600°C. After the gaseous effluent from the furnace was passed successively through a Hydro-Purge unit and a Dow gas purifier (Applied Science Laboratories, State College, Pennsylvania), it was passed through sintered glass frits in three scrubbing towers. One scrubbing tower contained 100 ml of reagent water, and the other two contained 100 ml of 0.1 M chromous chloride in 2.4 M hydrochloric acid with amalgamated zinc. The amalgamated zinc particles used were 0.8 to 3.2 mm in diameter for a Jones reductor (Fisher Scientific Company, Fairlawn, New Jersey). Details for preparing the chromous chloride scrubbers are given by Meites.[30]

Reagent-grade chemicals were used to prepare all solutions except the 1 M potassium chloride in the salt bridge with Vycor tip that isolated the reference electrode from the test solution. The 1 M potassium chloride was prepared from an "Ultrex" grade salt (Baker Chemical Company, Phillipsburg, New Jersey) by dissolving 7.45 g of the salt in reagent water and diluting the solution to 100 ml.

The 1 M sodium hydroxide electrolyte was prepared by dissolving 4.0 g of the salt in reagent water that had been boiled to remove carbon dioxide and diluting to 100 ml. One milliliter of this solution was diluted with 9 ml of reagent water to yield 0.1 M sodium hydroxide with a pH of 12.7. The pH was determined potentiometrically with a meter calibrated against a standard buffer with pH of 12.0 (Micro Essential Laboratory, Brooklyn, New York). The 0.1 M sodium hydroxide solutions with pH values of 13.2 and 11.7 were prepared by pipetting 10 ml of 1 M sodium hydroxide into two vessels to which about 50 ml of reagent water has been added, adjusting the pH of the solution in one vessel to 13.2 with 5 M sodium hydroxide and the pH of the solution in the other vessel to 11.7 with 6 M hydrochloric acid, and diluting to a final volume of 100 ml.

The 0.1 M EDTA solution was prepared by dissolving 7.44 g of disodium EDTA-2-water in reagent water and diluting to 200 ml. The

solution was heated as necessary to complete dissolution of the salt. The 1 M citric acid solution was prepared by dissolving 210 g of citric acid-1-water in reagent water with dilution to 1000 ml.

The 0.4 M citrate buffer with 0.02 M EDTA was prepared by mixing 400 ml of 1 M citric acid with 200 ml of 0.1 M EDTA, adding enough concentrated ammonium hydroxide (about 63 ml) to bring the pH to 5.0 while the solution was still hot, and after cooling, diluting to 1000 ml. Buffer solutions with pH values of 4.7 and 5.2 were prepared similarly by adjusting the pH with ammonium hydroxide before diluting. This solution was not sterilized by autoclaving for 15 min at 121°C and 1.03×10^5 Pascals (15 psi) because this treatment produced a polarographically active interfering species between -1.0 and -1.4 V vs. nce. New buffer solutions were prepared every two weeks.

DETERMINATION OF CHROMIUM(VI) BY DIFFERENTIAL PULSE POLAROGRAPHY

Exactly 9 ml of test solution and 1 ml of 1 M sodium hydroxide were pipetted into a 50-ml Pyrex beaker, mixed, and transferred to the polarographic cell. After deaerating the solution for 10 min with nitrogen gas treated to remove the oxygen, a differential pulse polarographic scan was made between -0.650 and -1.80 V vs. nce under suitable conditions. The peak for chromium(VI) appeared at about -1.14 V vs. nce. Typically, the height of the mercury column above the capillary from Sargent-Welch Company (part no. S-29419) was adjusted to about 45 cm to provide a natural drop time of about 2.8 s in 0.1 M sodium hydroxide (pH 12.7) at open circuit. The typical settings used for the PAR model 174 polarographic analyzer with mechanical drop timer were

drop time	1 s
scan rate	5 mV/s
display direction	positive
scan direction	negative
initial potential	-0.650 V
range	1.5 V
sensitivity	2 μA for 0 to 1 mg/l chromium(VI) 5 μA for 2 mg/l 10 μA for 5 mg/l 20 μA for 7.5 and 10 mg/l
modulation amplitude	50 mV
operation mode	differential pulse
output offset	negative settings as required

With the Houston omnigraphic 2200-3-3 recorder, the recorder Y-axis was adjusted to 1 V/in. (0.039 V/mm), and the X-axis was adjusted to 100 mV/in. (3.94 mV/mm). The Vycor tip of the 1 M potassium chloride salt bridge was stored in reagent water between experiments because dilute sodium hydroxide slowly dissolves Vycor.

DETERMINATION OF CHROMIUM(III) BY DIFFERENTIAL PULSE POLAROGRAPHY

Exactly 5 ml of test solution and 5 ml of 0.4 M ammonium citrate with 0.02 M EDTA were pipetted into a 50-ml Pyrex beaker, mixed, and transferred to the polarographic cell. After deaerating the solution for 10 min with nitrogen gas treated to remove the oxygen, a differential pulse polarographic scan was made between -1.00 and -1.40 V vs. nce under suitable conditions. The peak for chromium(III) appeared at about -1.26 V vs. nce. Typically, the height of the mercury column above the capillary from Sargent-Welch Company (part no. S-29419) was adjusted to about 45 cm to provide a natural drop time of about 2.8 s in 0.2 M ammonium citrate 0.01 M EDTA (pH 5.1) at open circuit. The typical settings used for the PAR model 174 polarographic analyzer with mechanical drop timer were

drop time	2 s
scan rate	2 mV/s
display direction	positive
scan direction	negative
initial potential	-1.00 V
range	1.5 V
sensitivity	1 μA for 0 to 1 mg/l chromium(III) 2 μA for 2 mg/l 5 μA for 5 mg/l 10 μA for 7.5 and 10 mg/l
modulation amplitude	50 mV
operation mode	differential pulse
output offset	negative settings as required

With the Houston omnigraphic 2200-3-3 recorder, the recorder Y-axis was adjusted to 1 V/in. (0.039 V/mm), and the X-axis was adjusted to 100 mV/in. (3.94 mV/mm). The Vycor tip of the 1 M potassium chloride salt bridge was stored in reagent water between experiments to prevent possible plugging of the tip.

SECTION 5

RESULTS AND DISCUSSION

Typical polarograms are given in Figure 1 for standard chromium(VI) concentrations under the conditions described in Section 4. With the mercury electrode adjusted to provide a natural drop time of 2.8 s in 0.1 M sodium hydroxide at pH 12.7, standard solutions of 0.05, 0.1, 0.3, 0.5, 1.0, 2.0, 5.0, 7.5, and 10.0 mg/l of chromium(VI) give peak currents of 0.04, 0.07, 0.30, 0.53, 1.2, 2.3, 5.8, 9.0, and 12 μA. No measurable current is observed for a reagent blank. The peak currents have been determined at -1.14 V vs. nce by measuring height above extrapolations of the current just before and just after the wave. Sensitivity is not improved by changing the scan rate from 5 to 2 mV/s, drop time from 1 to 2 s, and modulation amplitude from 50 to 100 mV. Improved sensitivity is expected according to a paper on instrumental artifacts in differential pulse polarography.[31]

Figure 2 gives the calibration curve for chromium(VI) for concentrations between 0 and 1 mg/l. The calibration curve for concentrations between 0 and 10 mg/l is given in Figure 3.

The detection limit from the pooled standard deviations of the current residuals and slope of the calibration curve for 0 to 10 mg/l of chromium(VI) given by Figure 3 is 0.13 mg/l at the 95 percent confidence level. This has been calculated by using a definition of detection limit given in the literature,[32,33]

$$st/k,$$

where

k = 1.20193, the slope of the least squares equation for Figure 3,

t = 2.365, the value for $t_{0.025}$ for n - 2 degrees of freedom equal to 7,

s = standard deviation for the current residuals from the least squares straight line ($i_p = 1.20193C - 0.061236$, where i_p = the least squares peak for each concentration, C).

Tests have been conducted with 0.50 mg/l of chromium(VI) solutions at pH 11.7, 12.7, and 13.2 in 0.1 M sodium hydroxide. Differential pulse polarograms for the test results are shown in Figure 4. The height and potential of the chromium(VI) reduction peak are nearly the same at pH 11.7 and 12.7. At pH 13.2 the peak height is the same as at pH 11.7 and 12.7, but the potential is -0.95 V vs. nce rather than -1.15 V. The peak potentials for chromium(VI) in a 0.1 M sodium hydroxide, illustrated by the bottom two differential pulse polarograms in Figure 4, are about 0.3 V more negative than those reported in the literature for 1.0 M sodium hydroxide.[15,17] The shift in peak potential at pH 13.2

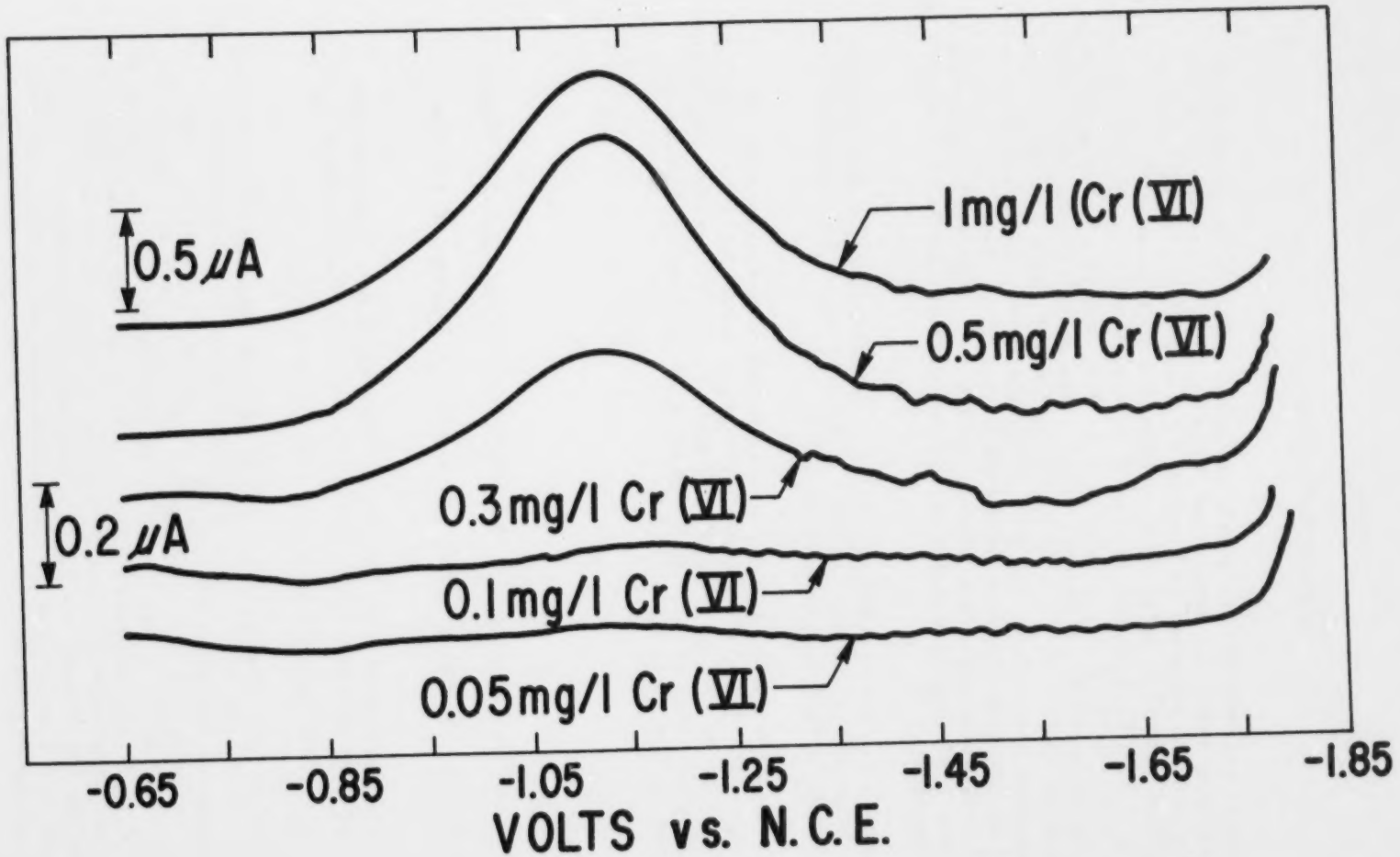

Figure 1. Typical differential pulse polarograms for standard chromium(VI) concentrations in 0.1 M sodium hydroxide at pH 12.7.

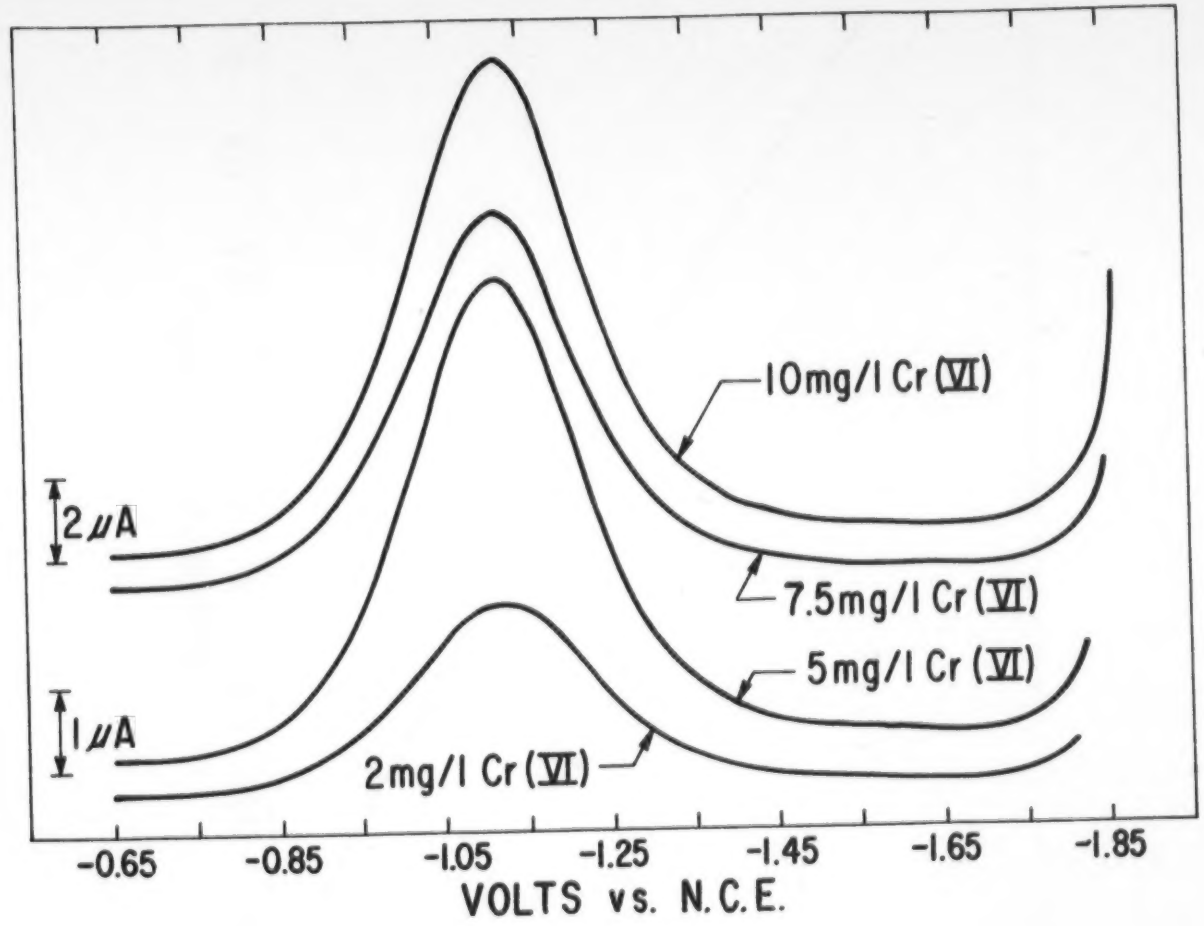

Figure 1 (continued)

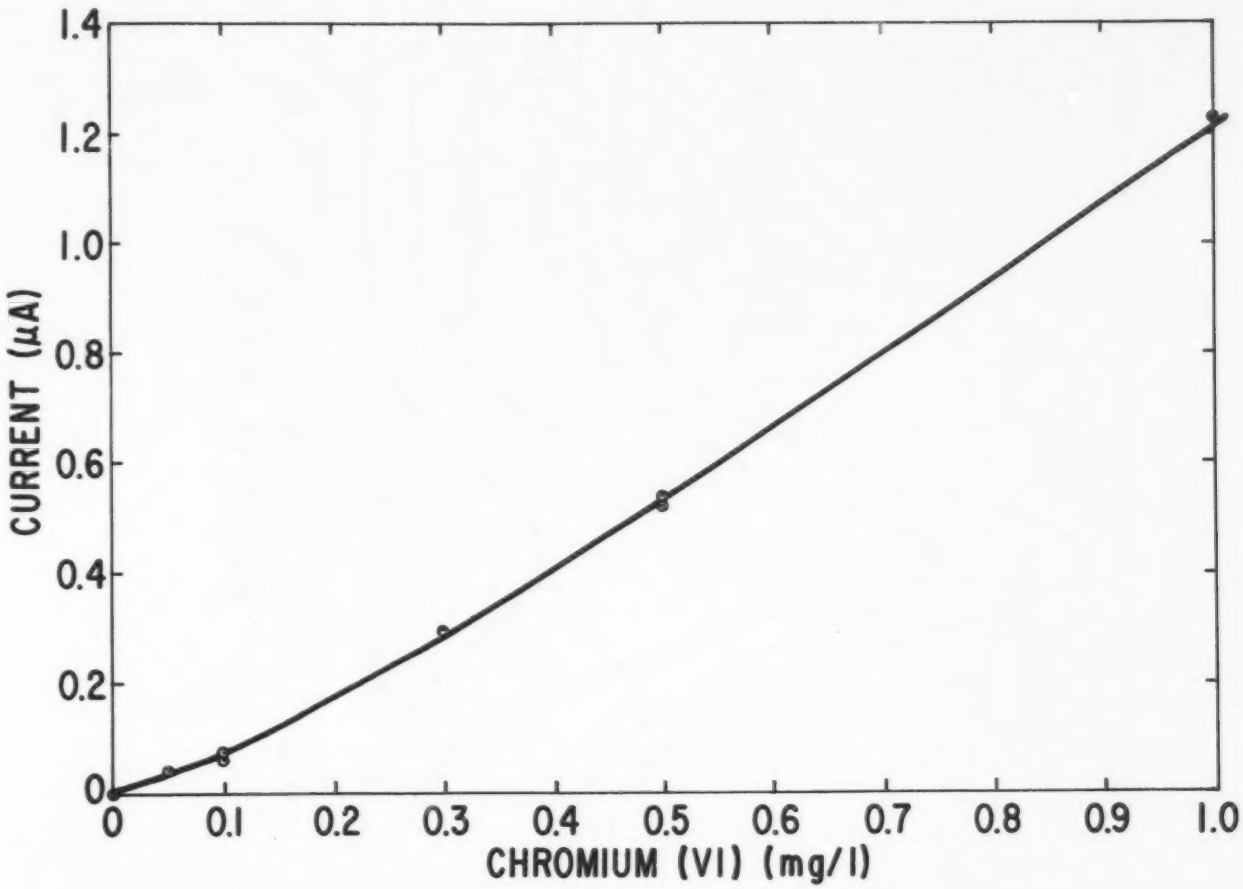

Figure 2. Calibration curve for 0 to 1.0 mg/l of chromium(VI) in 0.1 M sodium hydroxide at pH 12.7 by differential pulse polarography.

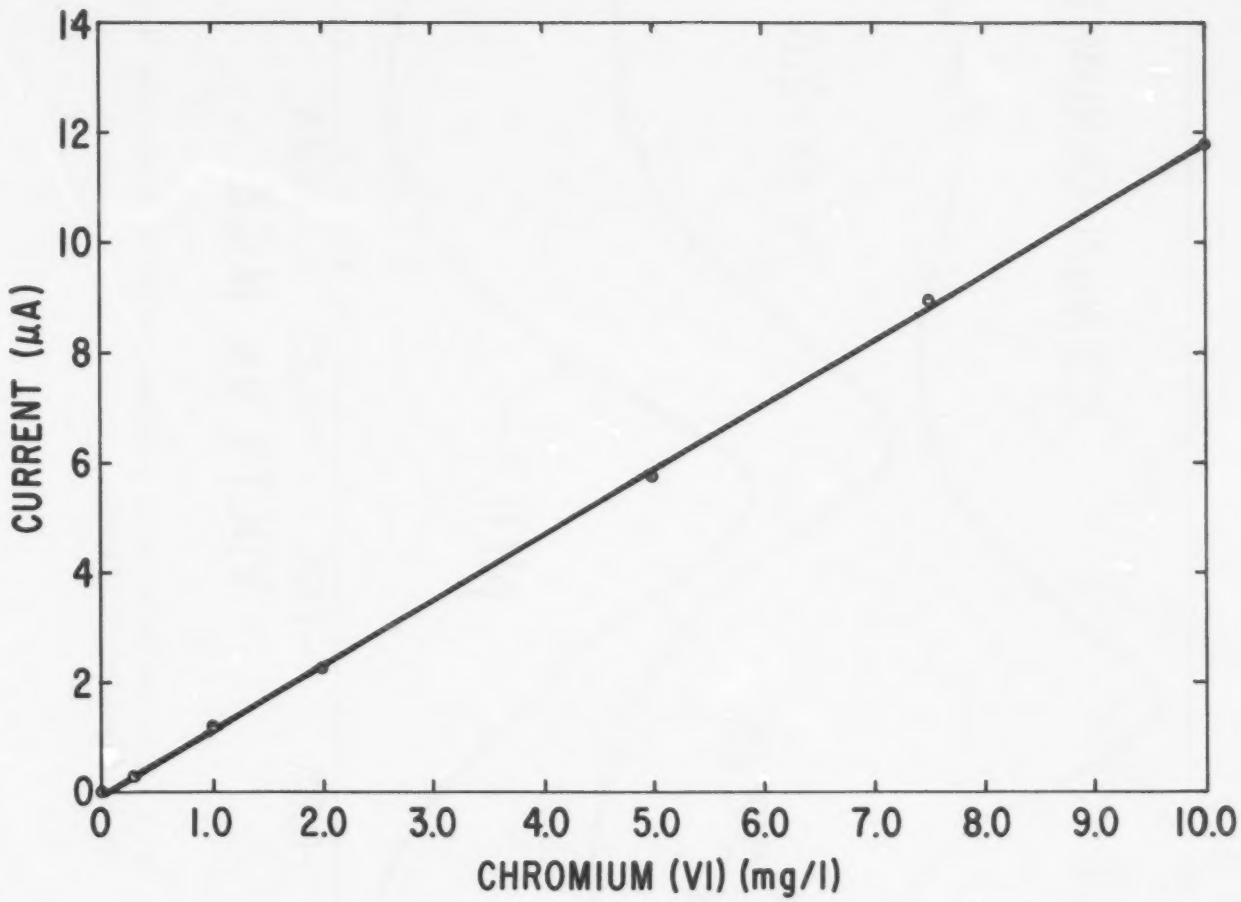

Figure 3. Calibration curve for 0 to 10 mg/l of chromium(VI) in 0.1 M sodium hydroxide at pH 12.7 by differential pulse polarography.

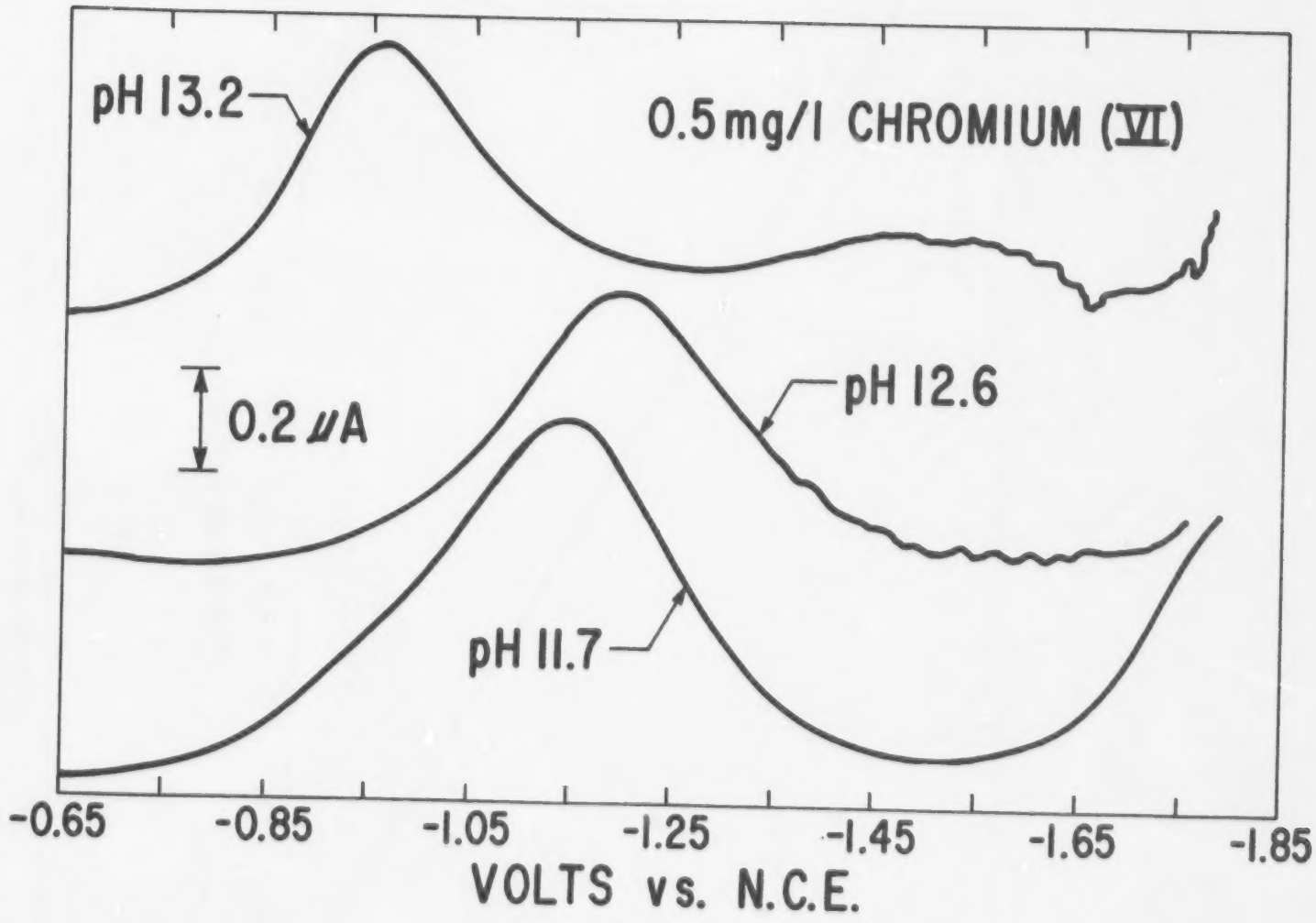

Figure 4. Peak shift caused by pH in differential pulse polarograms for chromium(VI) in 0.1 M sodium hydroxide.

could be caused by the higher ionic strength from the additional sodium hydroxide that is added to adjust the pH to 13.2.

Concentrations of 5.0 mg/l of zinc(II), copper(II), lead(II), chromium(III), and iron(III) do not interfere in the determination of chromium(VI) in 0.1 M sodium hydroxide at pH 12.7. Zinc(II) gives a peak nearby, but it does not affect the baseline above which extrapolations are made to measure the peak height for chromium(VI). Iron(III) causes only a slight elevation of the baseline, with a peak at -0.86 V vs. nce and twin peaks between -1.4 and -1.8 V vs. nce. Many natural waters contain zinc(II), copper(II), lead(II), chromium(III), and iron(III), but most of them contain these metals in concentrations of less than 5.0 mg/l.

Differential pulse polarograms of standard concentrations of chromium(III) under the conditions described in Section 4 are shown in Figure 5. With the mercury electrode adjusted to yield a natural drop time of 2.8 s in 0.2 M ammonium citrate with 0.01 M EDTA at pH 5.1, standard solutions of 0.05, 0.1, 0.3, 0.5, 1.0, 2.0, 5.0, 7.5, and 10 mg/l of chromium(III) produce peak currents of 0, 0.01, 0.09, 0.26, 0.63, 1.4, 3.7, 5.8, and 6.9 μA. No measurable current is observed for a reagent blank. The peak currents have been determined at -1.26 V vs. nce by measuring height above extrapolations of the current just before and just after the wave. The differential pulse polarograms have been recorded at a scan rate of 2 mV/s, a modulation amplitude of 50 mV, and a drop time of 2 s. Sensitivity is greater than at a scan rate of 5 mV/s and a drop time of 1 s. This agrees with theoretical considerations reported in the literature.[31]

Figure 6 gives the calibration curve for chromium(III) for concentrations between 0 and 1 mg/l. The absence of an appreciable response below 0.3 mg/l of chromium(III) may be caused by adsorption. The calibration curve for concentrations between 0 and 10 mg/l is shown in Figure 7.

Using the previously discussed criteria for chromium(VI), the detection limit from the pooled standard deviations of the current residuals and slope of the calibration curve for 0 to 10 mg/l of chromium(III) given by Figure 7 is 0.61 mg/l at the 95 percent confidence level. This has been calculated by using the same definition of detection limit that was used for chromium(VI).[32,33] The detection limit is

$$st/k,$$

where

k = 0.729001, the slope of the least squares equation for Figure 7,

t = 2.365, the value for $t_{0.025}$ for n - 2 degrees of freedom equal to 7,

s = standard deviation for the current residuals from the least squares straight line (i_p = 0.729001C - 0.0546954, where i_p = the least squares peak for each concentration, C).

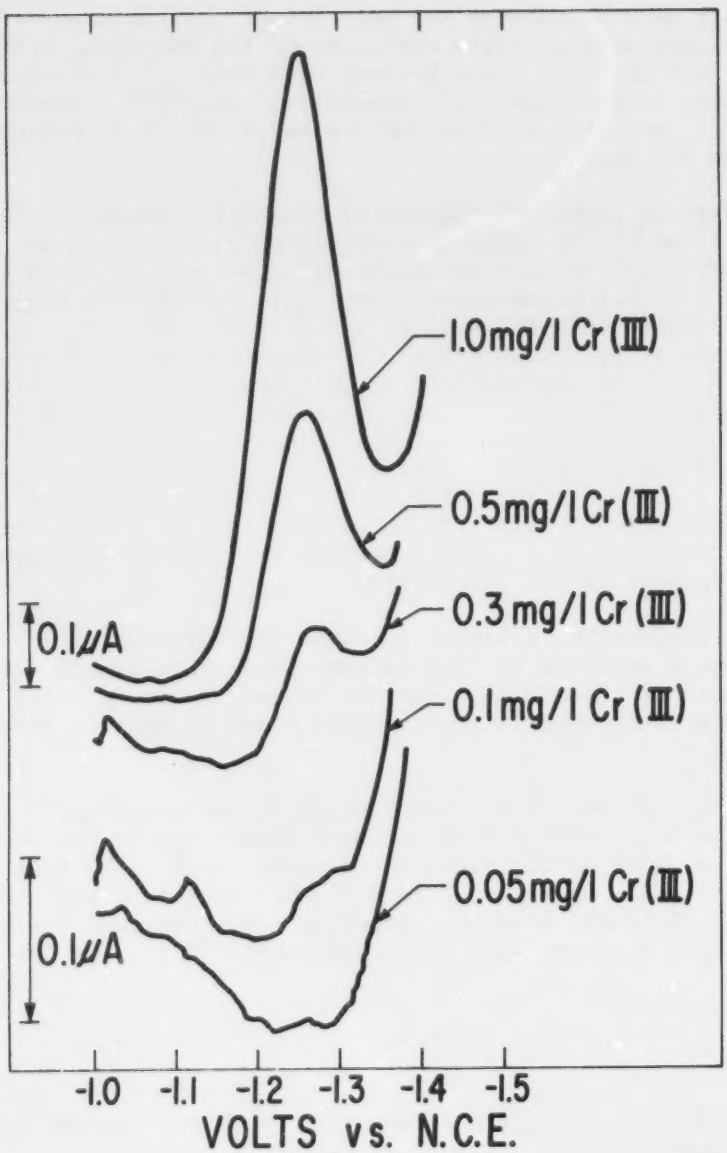

Figure 5. Typical differential pulse polarograms for standard chromium(III) concentrations in 0.2 M ammonium citrate with 0.01 M EDTA at pH 5.1.

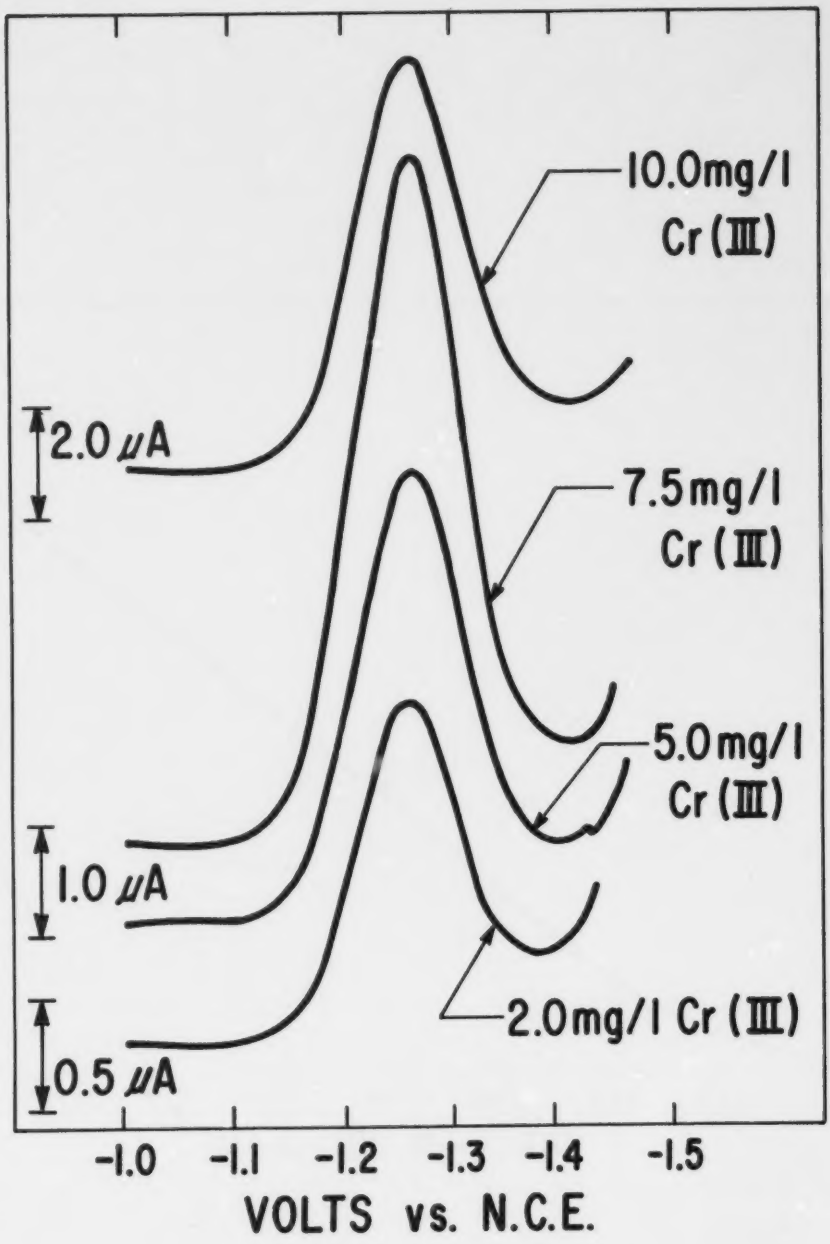

Figure 5 (continued)

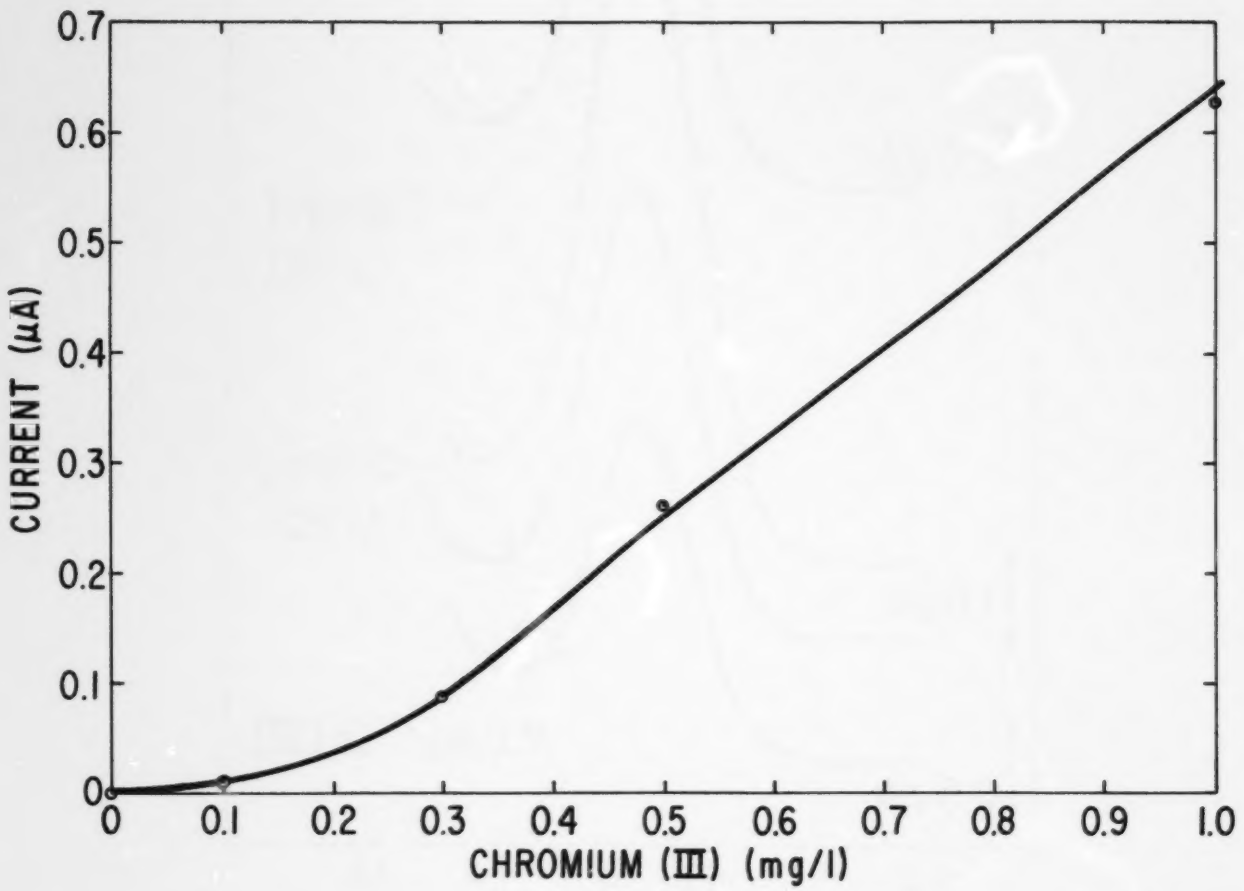

Figure 6. Calibration curve for 0 to 1.0 mg/l of chromium(III) in 0.2 M ammonium citrate with 0.01 M EDTA at pH 5.1 by differential pulse polarography.

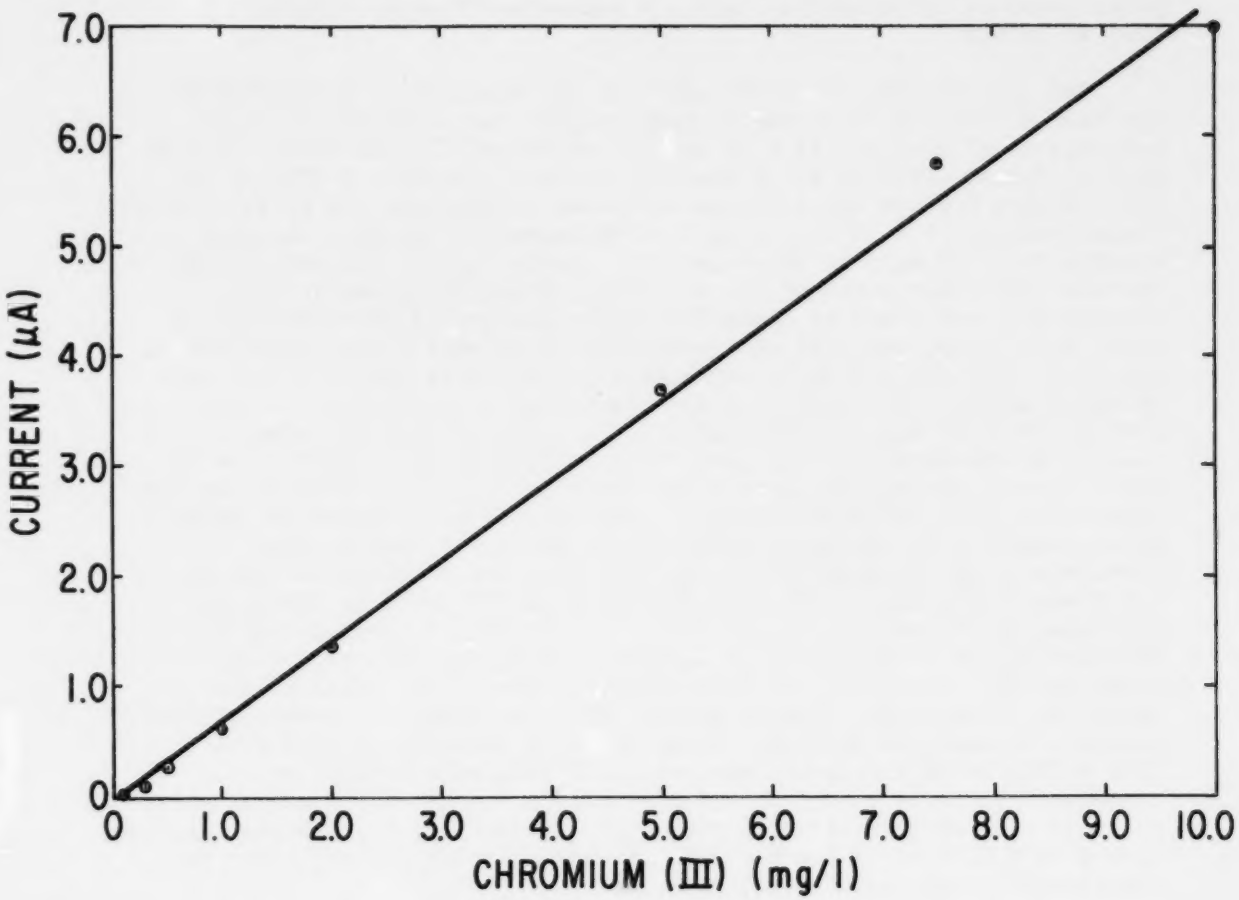

Figure 7. Calibration curve for 0 to 10 mg/l of chromium(III) in 0.2 M ammonium citrate with 0.01 M EDTA at pH 5.1 by differential pulse polarography.

The pH of the test solution affects the peak height of chromium(III). Tests have been conducted with 0.50 mg/l of chromium(III) solutions at pH values of 4.7 to 5.2 in 0.2 M ammonium citrate with 0.01 M EDTA. The potential of the chromium(III) peak is the same at pH values between 4.7 and 5.2. The height of the peak is the same at pH 4.7 and 5.0, but at pH 5.2 it is 43 percent of the value at pH 5.0. The decrease in pH from 5.0 to 4.7 increases the slope of the baseline just before and just after the peak. This obscures the peak for the determination of chromium(III) in the 0.2 M ammonium citrate with 0.01 M EDTA. This agrees with Zarebski's observations of pH in differential pulse polarograms of chromium(III) in 0.1 M potassium chloride with 0.01 M EDTA at pH 6.0.[24]

The interference of chromium(VI) in the analysis of chromium(III) has been determined by measuring peak heights for differential pulse polarograms of mixtures of 0.50 mg/l of chromium(III) and from 0 to 5.0 mg/l of chromium(VI) in 0.2 M ammonium citrate with 0.01 M EDTA at pH 5.0. Figure 8 gives the differential pulse polarograms for these mixtures. Concentrations of 0.50 to 5.0 mg/l of chromium(VI) increase the peak heights for 0.50 mg/l of chromium(III). Table 1 gives the raw current readings and composition of the mixtures. These increases in peak heights are equivalent to those for concentrations of chromium(III) of 0.06, 0.12, 0.30, and 0.88 mg/l caused by chromium(VI) concentrations of 0.5, 1.0, 2.0, and 5.0 mg/l, respectively. A concentration of 5.0 mg/l of chromium(VI) alone gives a peak height that is equivalent to that produced by 0.88 ppm of chromium(III). A graph of apparent concentration of chromium(III) for each concentration of chromium(VI) can be used, when necessary, to correct the chromium(III) concentration for the concentration of chromium(VI) that is determined by differential pulse polarography in 0.1 M sodium hydroxide at pH 12.7. Some of the interference by chromium(VI) in the determination of chromium(III) in 0.2 M ammonium citrate with 0.01 M EDTA at pH 5.0 could be caused by reduction of chromate by the metallic mercury that accumulates in the cell during the 15 min taken to deaerate and record the polarogram. Although this effect was not determined, Crosmun[19] has measured the amount of chromium(VI) reduced during the polarographic determination of chromate in ammonium acetate. Although 0.2 M ammonium citrate with 0.01 M EDTA at pH 5.0 is not entirely free from interference by chromium(VI), it is a much better electrolyte for the differential pulse polarographic determination of chromium(III) than 0.1 M potassium chloride with 0.01 M EDTA at pH 6.0 because, in this electrolyte, the peaks for chromium(III) and chromium(VI) coincide.[24]

Figure 9 gives the interference of 5.0 mg/l of zinc in the determination of chromium(III) when EDTA is not added to the 0.2 M ammonium citrate electrolyte at pH 5.0. A concentration of 5.0 mg/l of zinc produces a large peak that interferes severely at -1.26 V, the reduction potential for chromium(III). This figure also shows that 0.01 M EDTA eliminates interference by 5.0 mg/l of zinc.

Figure 10 gives interference of 5.0 mg/l of lead in the determination of chromium(III). As shown by this figure, the peak for lead appears at -1.19 V vs. nce with a height of 1.08 μA, which is equivalent to about 0.8 mg/l of chromium(III).

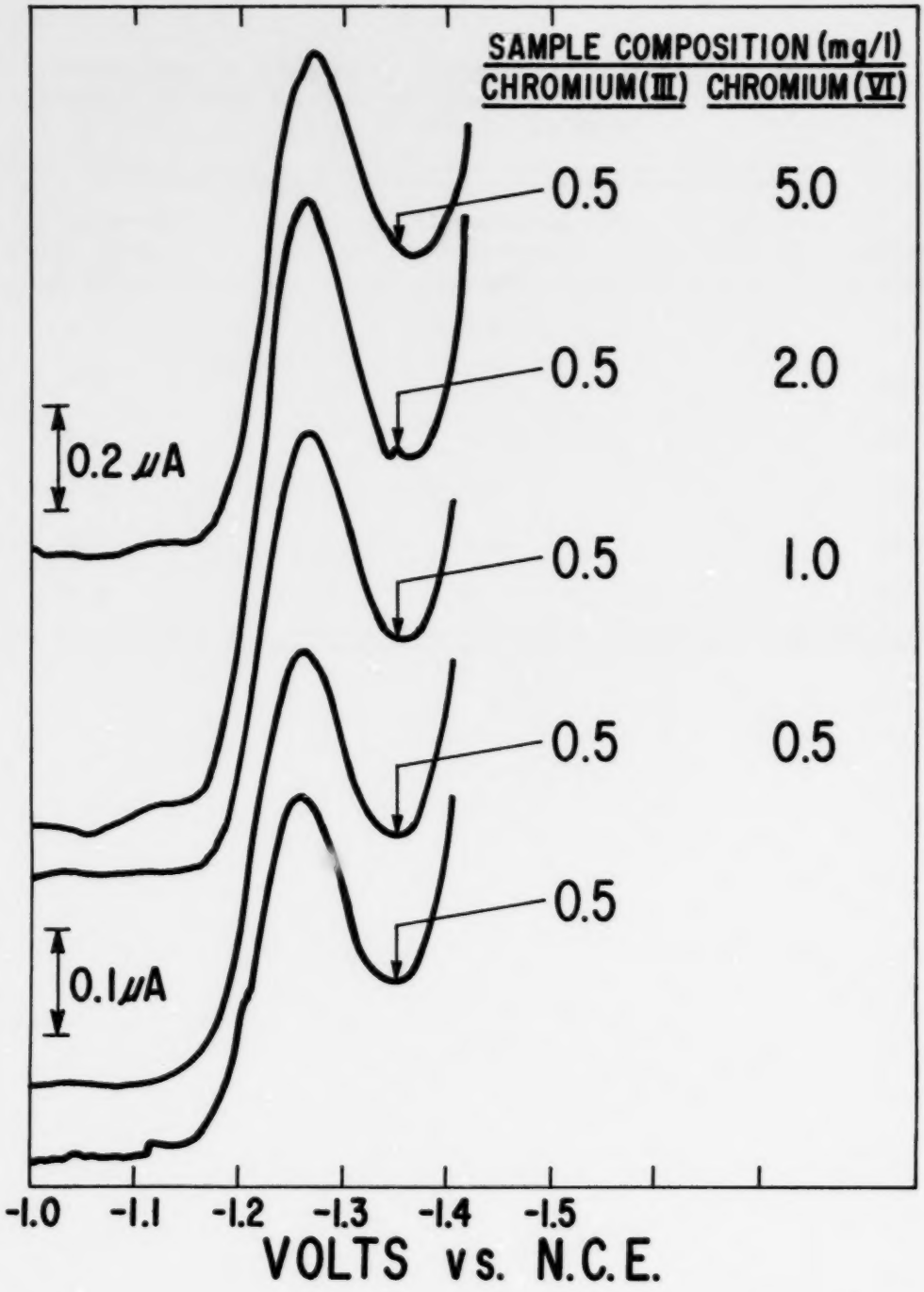

Figure 8. Interference of chromium(VI) in differential pulse polarograms for chromium(III) in 0.2 M ammonium citrate with 0.01 M EDTA at pH 5.1.

TABLE 1. EFFECT OF CHROMIUM(VI) IN ANALYSIS OF CHROMIUM(III) BY DIFFERENTIAL PULSE POLAROGRAPHY IN 0.2 M AMMONIUM CITRATE WITH 0.01 M EDTA AT pH 5.0

Current (μA)	Chromium(III) concentration (mg/l)	Chromium(VI) concentration (mg/l)
0.17	0.5	0
0.28	0.5	0.5
0.31	0.5	1.0
0.41	0.5	2.0
0.68	0.5	5.0
0.44	0	5.0

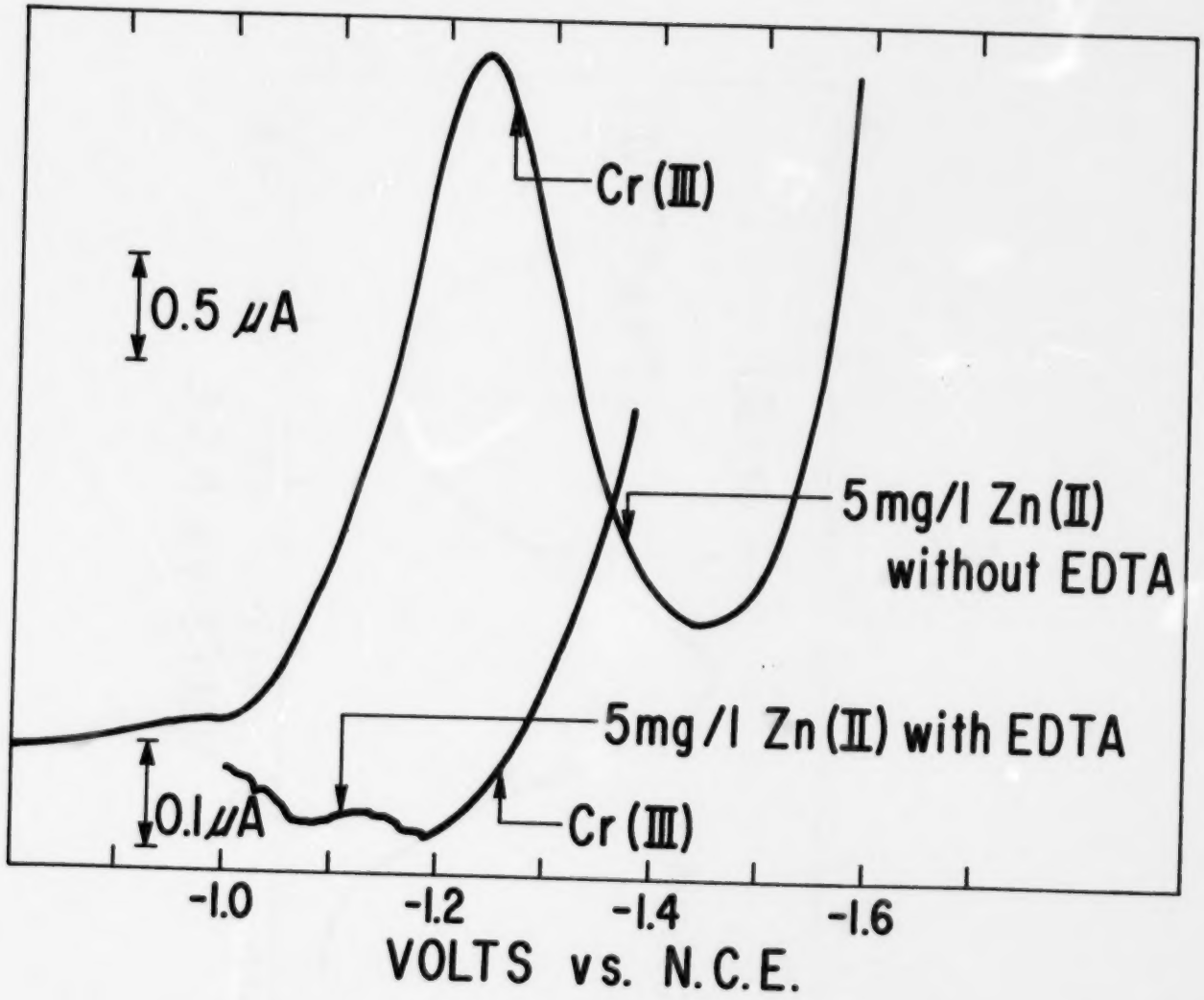

Figure 9. Use of EDTA to eliminate interference of zinc(II) in differential pulse polarograms for chromium(III) in 0.2 M ammonium citrate with 0.01 M EDTA at pH 5.0.

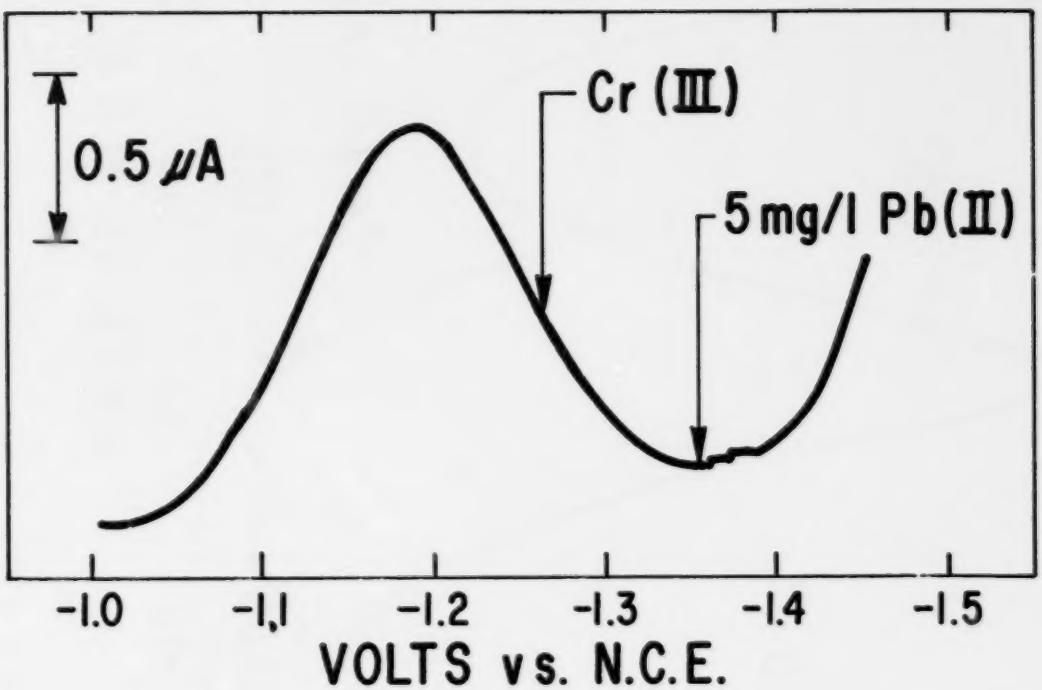

Figure 10. Interference of lead in differential pulse polarograms for chromium(III) in 0.2 M ammonium citrate with 0.01 M EDTA at pH 5.0.

Concentrations of 5.0 mg/l of iron(III), copper(II), and zinc(II) do not interfere in the determination of chromium(III) in 0.2 M ammonium citrate with 0.01 M EDTA at pH 5.0.

The detection limits of 0.13 mg/l for chromium(VI) and 0.61 mg/l for chromium(III) are not low enough to determine the expected concentrations of chromium species in most natural water samples. Also, interference in the determination of chromium(III) is greater than that for chromium(VI). But sample preparation with concentration by ion exchange,[26,34] solvent extraction,[27] precipitation,[27] or evaporation[18] should lower the detection limit as well as isolate the chromium species from potential interference.

Table 2 gives determinations of chromium(VI) and chromium(III) by the differential pulse polarography procedure described in Section 4 for triplicate solutions of spiked surface water for each individual species. The precision and accuracy based on the analysis of these three replicates, containing 0.55 mg/l of chromium(VI) and 0.99 mg/l of chromium(III), have been determined by comparison with a standard curve prepared by polarographing a series of standard solutions. The standard deviations are, respectively, 0.08 and 0.3 mg/l, the relative standard deviations are 19 and 34 percent, and the percentage accuracies are -24 and -12.[35]

The EPA trace metals reference concentrate 575 (No. 3)[28] has been assayed for chromium(VI) by the differential pulse polarographic technique described in this report. Exactly 10 ml of the concentrate was diluted to 500 ml rather than 1000 ml, and no additional acid was added. Triplicate results for chromium(VI) give a mean value of 0.19 with a standard deviation of 0.01.[35] The expected concentration for total chromium is 0.42, so by subtraction the remainder of the chromium is 0.23 mg/l of chromium(III). Attempts to verify this by differential pulse polarography led to high results for chromium(III), which are known to be caused partly by lead(II), as shown in Figure 10, and possibly by other elements in the reference samples that were not tested for interference in this study.

TABLE 2. DETERMINATIONS OF CHROMIUM(VI) AND CHROMIUM(III) BY DIFFERENTIAL PULSE POLAROGRAPHY FOR TRIPLICATE SOLUTIONS OF SPIKED SURFACE WATER[a]

Chromium(III) or chromium(VI) concentration (mg/l)	Chromium(VI) determination (mg/l)	Chromium(III) determination (mg/l)
0.55, Cr(VI); 0.99, Cr(III)	0.42 ±0.08[b] 0.41, 0.35, 0.50[c]	0.87±0.0.3[b] 1.16, 0.72, 0.72[c]

[a]Determination of chromium(VI) and chromium(III) was made by differential pulse polarography in 0.1 M sodium hydroxide at pH 12.7 and in 0.2 M ammonium citrate with 0.01 M EDTA at pH 5.0, respectively. Chromium(VI) determination was made in the filtrate from an aged surface water containing fungi and algae, while chromium(III) determination was made in fresh surface water.

[b]Average value and standard deviation for triplicate determinations.

[c]Individual values.

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LIST OF PRESENTATIONS

A speech, "Differential Pulse Polarographic Determination of Chromium(III) and Chromium(VI) in Water Samples," was given by Lyman H. Howe at the Fifth Annual Meeting, Federation of Analytical Chemistry and Spectroscopy Societies, Boston, Mass., October 30-November 3, 1978.